

THIRD QUARTERLY REPORT

for

DEVELOPMENT OF PILE TYPE, HIGH DISCHARGE RATE
NICKEL-CADMIUM SQUIB BATTERIES

SEPTEMBER 5, 1966 - DECEMBER 4, 1966

CONTRACT NO.: NAS5-10160

Prepared By

GULTON INDUSTRIES, INC.
ALKALINE BATTERY DIVISION
212 Durham Avenue
Metuchen, N. J.

For

GODDARD SPACE FLIGHT CENTER

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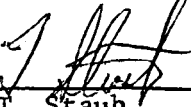
GULTON INDUSTRIES, INC.
ALKALINE BATTERY DIVISION
212 Durham Ave.
Metuchen, N. J.

for


GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland


Prepared By:


S. Charlip
Section Head
Engineering Development


T. Staub
Mechanical Engineer

Approved By:


H. N. Seiger
Director of Research


R. C. Shair
Vice President
Research & Development

DEVELOPMENT OF PILE TYPE, HIGH DISCHARGE RATE,
NICKEL-CADMIUM SQUIB BATTERIES

by

S. Charlip and T. Staub

ABSTRACT

The object of this report is to summarize the work and results accomplished during the past quarter in a program directed toward the design and development of a pile type, nickel-cadmium, squib battery.

Five-cell, pile type, nickel-cadmium batteries gave satisfactory performance when a sound seal was maintained between cells.

Mechanical sealing with "O" rings and "quad" rings, followed by encapsulation with potting compounds, was unsatisfactory.

Reliable seals were produced using adhesive bonding between the nickel substrate and uncured neoprene. The bond was formed during the vulcanization of the neoprene under heat and pressure.

The proper cleaning and conditioning of the electrodes' nickel surfaces is an important factor in achieving reliable bonds.

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INTRODUCTION

During the first and second quarters, primary efforts were directed in the areas of development of bipolar electrodes having circular shapes with .030 inch sinters.

The size, which would eventually go to make up a 5 cell battery, was to be determined from test discharges of single cells.

The objective of this program is to develop a 5 cell, bipolar, pile type, nickel-cadmium battery capable of 1 second, 10 ampere pulse discharge above 5.0 volts, with a capacity of 150 milliampere-hours at the 10 hour rate.

Test data obtained from single cells, published in previous reports, show that bipolar cells are capable of yielding the desired voltage at the 10 ampere rate in the flooded condition.

The results obtained from single cells were duplicated with 5 cell test modules when battery modules were properly sealed.

It is of great importance in this program to develop reliable sealing techniques, consistent with bipolar battery technology.

Initially, 5 cell modules were produced by sealing individual cells with "O" rings, and subsequently encapsulating the module in a suitable potting compound. The primary seal was made by the potting compound, while the "O" ring served to hold the electrolyte in the cell during the encapsulating process. However, problems were encountered in maintaining the electrolyte in the cells during the encapsulation. Effecting a bond between the potting compound and the nickel proved difficult under these conditions.

During the past quarter, efforts were concentrated on the techniques and materials for adhesive bonding of rubber to the nickel substrates of cells as primary seals. The techniques for introducing electrolyte into each cell would depend on the sealing techniques used. Previous tests have shown that bipolar cells and batteries gave satisfactory performance when the right amount of electrolyte and pressure on the cells was present.

Several sealing methods, materials, and techniques were tested and evaluated. The results are described in the body of this report.

TECHNICAL DISCUSSION

"O" Ring And "Quad" Ring Seals

Test data obtained from the discharge of 5 cell bipolar batteries, discussed in the Second Quarterly Report, show that bipolar batteries are capable of the 1 second-10 ampere pulse discharge above 5 volts. The capacity requirements of 150 milliampere-hours have been exceeded with each electrode size tested.

Electrodes with 2.76 to 3.14 square inches of active area have been shown to meet the pulse requirements in single cells. Five cell battery modules have, likewise, met the requirements when the module seal held up during the charge-discharge cycling.

The five cell batteries, however, developed leaks through the encapsulating compound after several charge-discharge cycles. The same potting compounds used to encapsulate the batteries were successfully used in similar battery applications where the substrates were either of carbon steel or stainless steel.

An examination of the mode of failure revealed the absence of a reliable bond between the nickel substrate and the encapsulating compound. The "O" rings also failed to contain the electrolyte in the cells during cycling.

An elastometer type seal known as "Quad-Ring Seal", manufactured by the Minnesota Rubber Co., Minneapolis, Minnesota, was thought to merit investigation. This seal makes a 2 point contact with a sealing surface, twice the number of sealing surfaces as an "O" ring. The relative square cross-section of the "quad" ring and flexibility of the four lobed seal makes it easier to apply pressure to the cell stack and obtain intimate contact between separator and electrodes, for lower cell impedance. A cross-sectional view of a bipolar cell assembled with a "quad" ring is shown in Figure 1.

One five cell battery was constructed using "quad" ring seals. This battery was assembled of bipolar electrodes with a sinter area of 2.40 square inches (1-3/4 dia.). However, to give the cell more free volume and to compensate for the effects of concentration polarization, the negative side of the sinter was cut down to 1-5/8 diameter. This gave it an active area of 2 square inches. The battery thus constructed had a free cell volume equal to the difference of the positive electrode (2.40 in^2) and negative electrode (2.07 in^2), times the thickness of one electrode (.030 inch), or approximately 0.16 cc.

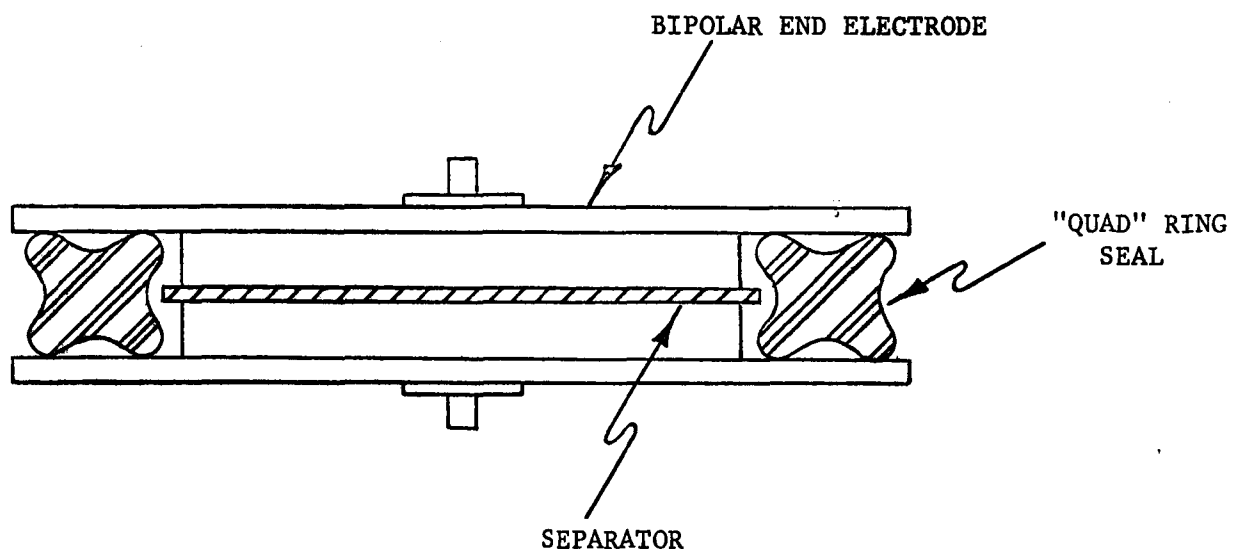


FIGURE 1. CROSS-SECTIONAL VIEW OF A BIPOLAR CELL ASSEMBLED WITH A "QUAD" RING SEAL

The total volume of electrolyte in one cell varies from 1.5 to 2.0 cc per cell. A free volume of 0.16 cc, or about 10% of the electrolyte volume, should improve the charging characteristics of the cell, particularly with regard to overcharge capability.

The battery was assembled using "quad" rings and was encapsulated in a potting compound.

After one formation cycle, the battery was pulsed across a 0.49 ohm load for six consecutive one second pulses. The results are shown in Figure 2. These results are identical with those previously obtained from 5 cell bipolar batteries with 2 in² of active area. The voltage on the first pulse was 4.9 volts.

Following the pulse discharges, the battery was given a constant current charge of 15 milliamperes. After sixteen hours of charging, a small electrolyte leak was observed emanating from the junction of the positive stud and potting compound. The battery was taken apart and examined for causes of failure. It was found that the leak occurred from one cell, the end cell, where the electrolyte had penetrated the bond between the potting compound and the end plate.

A second five cell battery was assembled. The electrode sizes of both the positive and negative sinters were 2-1/4" in diameter (4 in² of active area). The nickel substrates were thoroughly cleaned, sand blasted, wiped down with MEK, and washed and dried. The electrolyte was introduced into each cell prior to assembly by wetting the 7 mil, non-woven nylon separator with KOH and wetting the sinters with the balance until it was all absorbed. The edges of the nickel substrate were again cleaned with a mild solution of boric acid, washed and dried. A "quad" ring, coated thinly with Kel-F grease, was placed between each cell. The entire 5 cell module was then placed into a tightly held mold and encapsulated with a potting compound, ERL-2795, manufactured by Union Carbide Co. After the potting compound solidified, the battery was removed from the mold and restrained between two lucite sheets, 1/2 inch thick, and placed on charge at the 20 mA constant current rate.

Prior to pulsing at the 10 ampere rate, the battery was given one discharge at 600 mA to one volt. The capacity above 1.0 volt was 570 mAh.

The battery was given a second charge and pulsed at 10 A for one second. The voltage and current were recorded on an oscilloscope. The oscilloscope traces of the pulse discharge are shown in Figure 3.

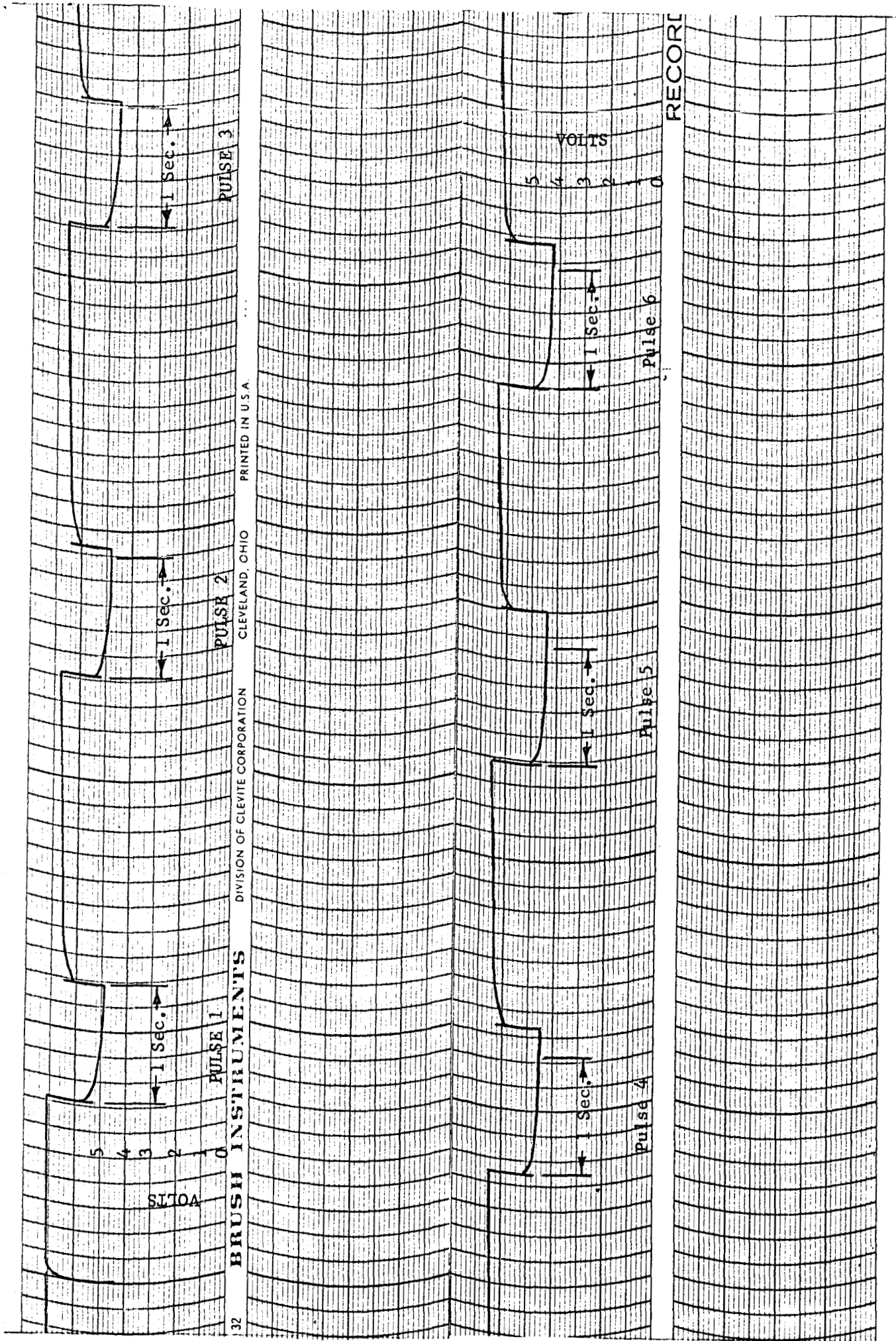


FIGURE 2. PULSE DISCHARGES FOR A 5 CELL BIPOLAR BATTERY WITH 2.40 IN² POSITIVE AND 2.07 IN² NEGATIVE ACTIVE PLATE AREAS

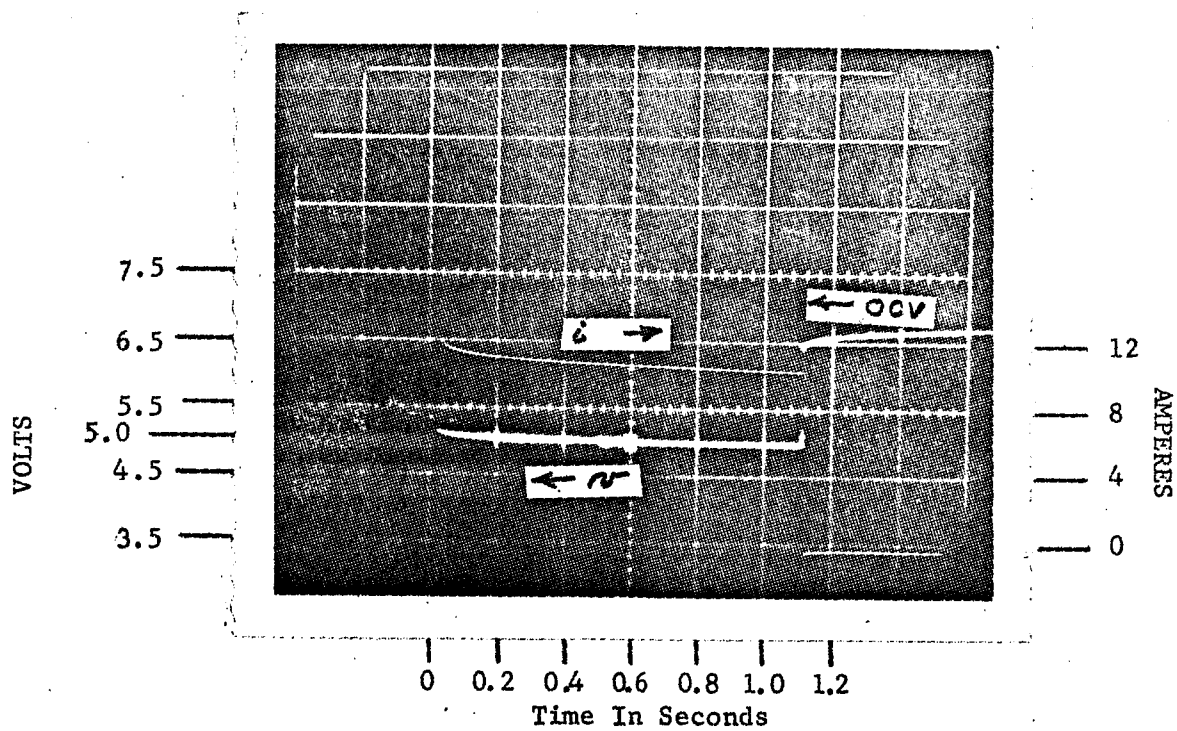


FIGURE 3. OSCILLOSCOPE TRACES FOR A PULSE DISCHARGE OF A 5 CELL, 4 IN² BIPOLAR BATTERY

The voltage at the 10 ampere pulse was at the 5 volt level for the large 4 in² bipolar battery.

It was felt that, even though no leaks were immediately observed, this method of sealing offers no measure of reliability, and other techniques would have to be developed to obtain a reliable seal.

Adhesive Bonding

The application of a rubber-to-metal adhesive bond in the assembly of bipolar batteries suggested itself when other means failed to produce reliable seals.

The joint geometry is particularly adaptable for adhesive bonding since the substrate is an ideal lap joint in tension, with the stress (generated by the cell pressure) perpendicular to the plane of the joined surfaces.

With proper assembly techniques, cleavage and peel stresses can be minimized. The added support of the encapsulating compound would contribute to uniformity of stress distribution across the adhesive joints and prevent peeling tendencies caused by the tensile stresses in the free edges of the adhesive joints.

Surface Treatment

An important aspect of adhesive bonding is the surface preparation and treatment prior to making the joint. Adherent surfaces must be pre-treated and kept clean until bonded.

Although the forces which produce adhesion between organic materials and metal surfaces are not clearly understood, it is known that these forces are short-range with respect to molecular dimensions. Therefore, the presence of foreign substances will interfere with the close approach, or intimate contact between adhesive and adherent, and will result in lower surface energy and poor bond.

Three methods for cleaning the surface of the nickel substrate were considered: chemical, mechanical abrasion, and degreasing. With some variations in procedures, the latter two were employed. The chemical cleaning was not considered practical. The recommended composition of the etchant for nickel is a strong concentration of nitric acid. This was not considered practical in view of the fact that bipolar electrodes were fully impregnated, and the presence of acid in the sinter could not be tolerated nor effectively neutralized.

A flow chart of the cleaning methods used, and found to be practical for this application, is shown in Figure 4.

Sand blasting was considered the most practical method of mechanical abrasion. The electrodes were placed in a fixture, masking the sinteres, and only the bonding edges were exposed to the abrasives. A uniform surface roughness was thus obtained. The roughness factor of the nickel substrate is considered to be significant in obtaining a good joint. A uniformly roughened surface will possess a larger

actual area for the action of molecular forces. The roughening is usually accompanied by an increase in the free surface energy produced through working of the surface and through the higher surface energy property possessed by rough metal crystals.

To test the surface for proper preparation and cleanliness, each electrode was given the "water break" test. A droplet of distilled water was placed on the cleaned surface and observed if it spread and wet the surface smoothly. It was felt that if a drop of distilled water wets the metal surface and spreads smoothly over the surface, without breaking up into individual droplets, the surface could be presumed to be free of harmful organic films. A surface which is uniformly wet by distilled water will probably also be wet by the adhesive. The surfaces were thoroughly dried after each test.

Adhesives and Seal

Several known organic compounds were tested as a rubber-to-metal adhesive. The adhesives that were recommended for bonding nickel-base alloys are in a class known as thermosetting adhesives. These undergo chemical changes during the curing cycle and effect a bond between the rubber and metal. The adhesive sought for this application, initially, was one requiring the minimum curing temperature. Since the electrodes to be bonded are impregnated with active materials, adhesives with room temperature curing cycles were sought, to minimize the heat effect on the active materials and cell function.

A list of bonding agents, curing at room temperature, was tested and evaluated. In each case, the bond failed to hold up when subjected to KOH environment.

It was apparent that reliable bonds to nickel could not be achieved with the room temperature curing adhesives and that thermosetting adhesives would have to be adopted.

The major problem was to localize the heat around the flange and to limit the temperature for the entire electrode to 300°F.

A combination of adhesives manufactured by Hughson Chemical Co. showed promising results. Several cells were assembled using a primer and adhesive. The primer was Chemlock 205 and the adhesive, Chemlock 220.

The 205 primer was applied to a cleaned and conditioned nickel substrate and allowed to air dry for 20 minutes, to vaporize the solvents which are commonly found in adhesives. On many occasions, the presence of solvents in adhesives and their inability to escape from the bonding surfaces, resulted in extended cure time and porous bonds.

The rubber seal used to bond to the surface was a cured neoprene washer, 45-55 durometer, manufactured to Spec. MIL-R-3065. The gasket was soaked for one minute in a 10% solution of Hughson 220 adhesive (one part 220 and 9 parts MEK) and placed over the primed surfaces of the substrate.

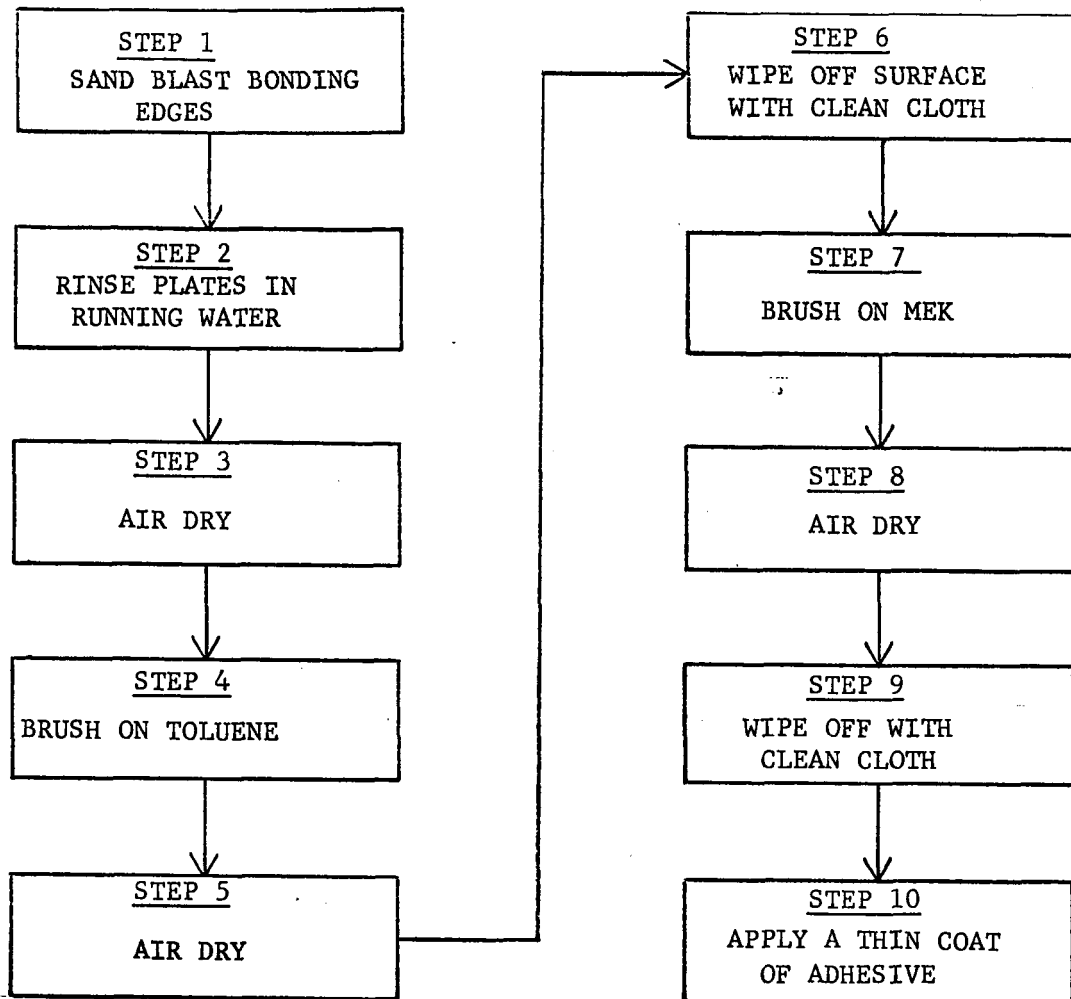


FIGURE 4. FLOW CHART FOR SURFACE PREPARATION OF NICKEL SUBSTRATES FOR BIPOLAR BATTERIES

The assembly was clamped between two rings and placed into a hydraulic press with heated elements. The temperature was maintained at 300°F for one hour on the pressure rings. The pressure was 1000 lb/in².

The bonded half-plates were assembled into a bipolar cell by flooding the inside with KOH. The rubber-to-rubber bond between the cell halves was accomplished using a neoprene cement. A cross-sectional view of the cell is shown in Figure 5.

The test cell was subjected to temperature cycling between 73°F and 150°F for 32 hours, after which the cell was placed on the shelf for 2 weeks. At the end of this period, the cell showed no signs of leaking.

The cell was taken apart by prying open the seal. There was evidence of interface attack and a joint weakening where the primer was applied. The areas free of the 205 primer were solidly bonded.

In a parallel program, several cells and two 5 cell batteries, with 2-1/4 inch diameter sinter area, were built using uncured neoprene #1450B, 40 durometer, manufactured by Niagara Rubber Co., Plainfield, N. J., in lieu of the cured neoprene washers. The bonding adhesive was Hughson 220, which was applied to the cleaned and conditioned nickel substrate and air dried for 30 to 60 minutes. The uncured neoprene was placed on both parts of a set of matching steel molds and applied over both substrate edges of the bipolar electrode. The entire package was placed in a hydraulic press with heated elements and maintained for 20 minutes at a temperature of 300°F and 1500 lb/in² of pressure. A photograph of the press is shown in Figure 6.

Upon air cooling, the edges of the electrode were trimmed of the excess neoprene, and the electrode was ready for assembly, as previously described. Figure 7 shows a half mold for vulcanizing seals.

The bonds obtained between the rubber and the metal during vulcanization have been tested and found to be superior to those previously obtained without vulcanizing.

The bonded 5 cell module was then encapsulated in a potting compound, ERL-2795, manufactured by Union Carbide. The batteries, so assembled, showed no trace of leakage when subjected to overcharge regimes. Subsequent destructive tests showed that the bonds were stronger than the rubber when subjected to peel and tensile tests. Cells subjected to simulated cell environment held up well with no signs of bond weakening.

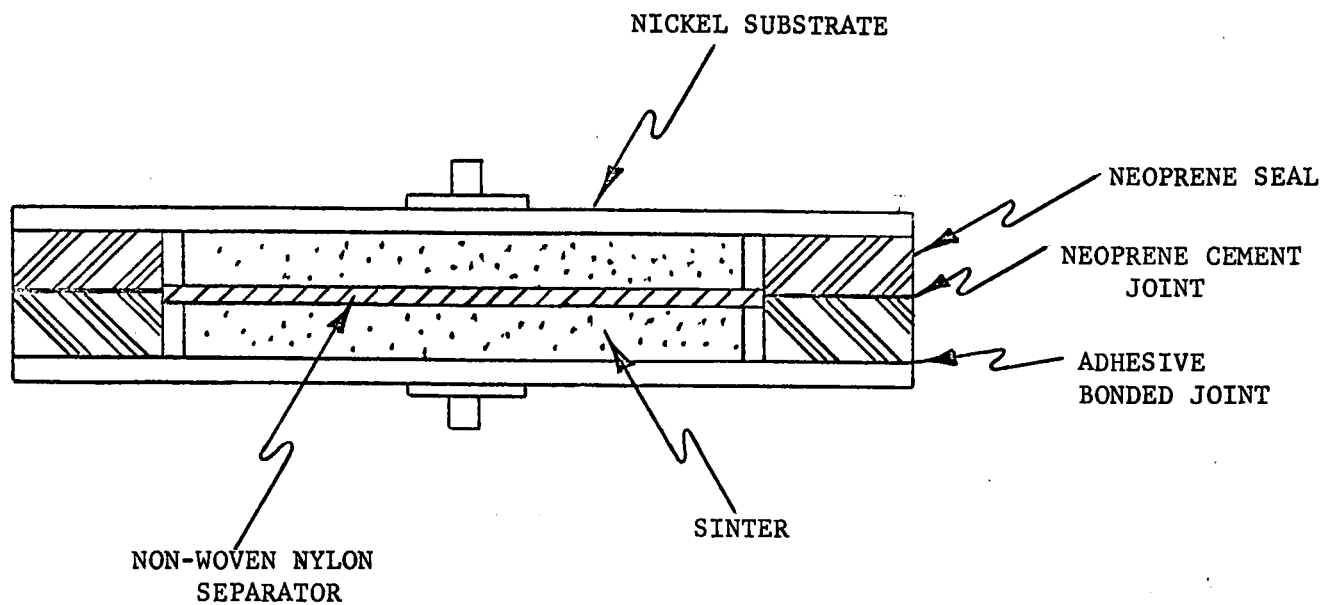


FIGURE 5. CROSS-SECTIONAL VIEW OF A RUBBER-TO-METAL
SEAL IN A BIPOLAR CELL

THE SEAL WAS CURED NEOPRENE



FIGURE 6. WABASH PRESS WITH HEATED PLATTENS FOR
 VULCANIZING RUBBER SEALS

 OPERATOR LOADING ELECTRODES

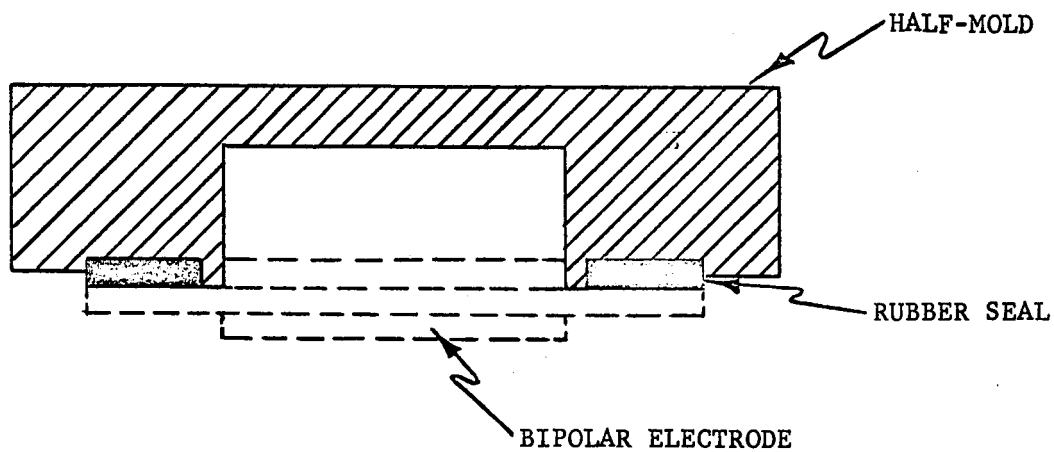


FIGURE 7. HALF-MOLD FOR VULCANIZING RUBBER SEAL
TO SUBSTRATE OF BIPOLAR ELECTRODE

DISCUSSION OF RESULTS AND CONCLUSIONS

Based on the results and engineering evaluation of the process, the method of sealing bipolar cells, using rubber to metal adhesive bonding, appears to be satisfactory.

A most important aspect of the bonding process is the proper cleaning, preparation, and surface conditioning (roughing) of the nickel surface. Methods developed in this program show satisfactory results and can be applied to production lots.

Using these sealing methods, 5 cell bipolar batteries will be constructed and evaluated for performance to the specified requirements.

The progress of this work and the test results will be discussed in the next report.

WORK PLANNED

TASK III

1. Fabricate, test, and evaluate performance of 5 cell batteries.
2. Determine charging rates and overcharge capabilities.
3. Build 10 batteries for delivery to NASA.